PATENT SPECIFICATION 1,083,910

NO DRAWINGS.

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1,083,910

Date of filing Complete Specification: Aug. 22, 1966.

Application Date: Sept. 28, 1965. No. 41201/65.

Complete Specification Published: Sept. 20, 1967.

Index at Acceptance:—C2 C2B56.

Int. Cl.:—C 07 c 119/04.

COMPLETE SPECIFICATION.

Distillation of Organic Polyisocyanates.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the production of organic polyisocyanates in particular to the recovery of organic polyisocyanates by distillation from crude mixtures containing the said polyisocyanates.

It is well known to manufacture organic polyisocyanates by reaction of primary amines or their salts with phosgene and although other methods of producing polyisocyanates are known, the phosgenation of primary amines or their salts is the method commonly used on the industrial scale. Manufacture is often carried out in the presence of an inert organic diluent.

In the manufacture of organic polyisocyanates by any of the known methods and during the subsequent step of recovering the organic polyisocyanate from the reaction mixture, a process usually involving distillation, by-products such as ureas, biurets and polymers are formed, resulting in a lower yield of the polyisocyanate than would otherwise be expected. During recovery of the diisocyanate by distillation the by-products formed during the reaction and distillation, concentrate in the distillation residue and remain after distillation as an intractable residue which tends to retain a further quantity of polyisocyanate and prevent its recovery by distillation.

Many attempts have been made to overcome this problem and to increase the yield of polyisocyanate but none have proved entirely satisfactory. For example the use of specialised distillation equipment has been proposed; the addition of materials such as high boiling polyethers and hydrocarbons to the polyisocyanate in order to liquify the residue has also been proposed. It has however been found necessary to use comparatively large amounts of such materials and their recovery and re-use has been found difficult.

It has now been found that an increased yield of polyisocyanate is obtained if there is added to the crude polyisocyanate before distillation a small proportion of a polyalkylene polyether and the said distillation is then carried out from an agitated thin film of the crude mixture. Distillation from an agitated thin film of the crude polyisocyanate/polyalkylene ether mixture may be conveniently carried out in a thin film evaporator or similar apparatus many types of which are available commercially.

Thus according to the present invention there is provided a process for the recovery of organic polyisocyanates from crude mixtures containing said polyisocyanate which comprises mixing a polyalkylene polyether with said crude mixture and distilling the organic polyisocyanate from an agitated thin film of the so-formed mixture of crude polyisocyanate and polyalkylene polyether.

The recovery process of the present invention may be applied to any distillable organic polyisocyanate including aliphatic, aromatic, aliphatic/aromatic and heterocyclic polyisocyanates. Although the process is applicable to crude mixtures containing organic polyisocyanate however these mixtures have been prepared, it is particularly applicable to crude mixtures which are the product of the reaction of a primary polyamine or a

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salt thereof with phosgene, that is the crude organic polyisocyanate or solution thereof which is produced by phosgenation of a primary polyamine or its salt. The phosgenation of primary polyamines and their salts is often carried out in an inert organic diluent; the present recovery process may be applied to the product of the phosgenation without any prior removal of the inert organic diluent or a portion or the whole of the diluent may be removed, for example by distillation, before application of the present recovery process. If the present process is applied while all or part of the inert organic diluent is still present, the diluent may be distilled with the polyisocyanate, the polyisocyanate can then be easily separated from the diluent by a further distillation since the undesired by-product will have been removed in the prior distillation.

Suitable inert organic diluents commonly-employed in organic polyisocyanate manufacture include esters, hydrocarbons and halogenated hydrocarbons, examples of which include mono- and di-chlorobenzenes, chlorotoluene, carbon tetrachloride, trichlorofluoromethane, toluene, xylene, butyl acetate, hexyl acetate, ethyldimethylcarbamate and dimethyl and diethyl carbonates.

Examples of organic polyisocyanates to which the present process can be applied include tetramethylene diisocyanate, hexamethylene diisocyanate, tolylene-2,4 and 2,6-diisocyanates and mixtures thereof, diphenylmethane-4,4¹-diisocyanate, meta- and para-phenylene diisocyanates, 1-methylcyclohexane-2,4-diisocyanate, chlorophenylene-2,4-diisocyanate, para-isocyanatobenzyl isocyanate, 1,5-diisocyanatonaphthalene and 4,4¹-diisocyanato-dicyclohexylmethane.

The process is particularly applicable to aromatic polyisocyanates especially tolylene diisocyanate.

Polyalkylene polyethers which may be employed in the present process are well known in the art and are made by the addition polymerisation of 1,2-alkylene oxides to compounds containing at least one active hydrogen atom. Suitable 1,2-alkylene oxides from which the polyalkylene polyethers may be made are ethylene oxide, 1,2-propylene oxide, 2,3-butylene oxide and the like. Preferred polyalkylene polyethers are those based on 1,2-propylene oxide. Polyethers based on mixtures of alkylene oxides, for example ethylene oxide and propylene oxide may be employed.

Compounds containing at least one active hydrogen atom which are suitable starting materials for the preparation of the polyalkylene polyethers used in the present process include water, aliphatic monohydric alcohols such as ethyl alcohol, propyl alcohol and octyl alcohol (octanol), ethylene glycol, propylene glycol, 1,4-butanediol, diethylene glycol, triethylene glycol, triethylol propane, glycerol, and aliphatic and aromatic mono- and polycarboxylic acids such as acetic acid, succinic acid and benzoic acid.

Thus examples of polyalkylene polyethers which may be used in the present process include polyethylene glycols, polypropylene glycols and condensation products of ethylene and propylene oxides with aliphatic alcohols, aliphatic diols and triols, aliphatic and aromatic mono- and polycarboxylic acids.

Although the hydroxyl group present in the above polyalkylene polyethers may be etherified or esterified we prefer to use polyalkylene polyethers which contain at least one hydroxyl group. We also prefer to use polyalkylene polyethers in which the polyalkylene moiety is derived from 1,2-propylene oxide, that is polyethers such as polypropylene glycol and propylene oxide condensates of aliphatic alcohols, diols and triols.

The amount of polyalkylene polyether to be used in the present process is considerably smaller than has previously been suggested in recovery processes involving the addition of additives to an organic polyisocyanate and is generally less than 10% of the weight of the polyisocyanate. It is preferred to use from 1% to 5% of polyalkylene polyether based on the weight of tthe polyisocyanate.

Distillation of the polyisocyanate from an agitated thin film of the crude polyisocyanate/polyalkylene polyether mixture may be carried out in any of the known types of distillation or evaporation equipment adapted for distillation from an agitated thin film of liquid. Such distillation equipment is generally described as a thin film evaporator and although the various types may differ the basic principle of operation is the same. The liquid being distilled is allowed to flow in the form of a thin film over a heated surface, generally the inside surface of a cylindrical or conical tube, the film being agitated by blades mounted on a rotating spindle forming the central axis of the tube. The blades may agitate the surface of the thin film by passing over or contacting the surface or they may actually wipe the walls of the tube keeping the whole film in constant motion. In the latter case the evaporator is known as a wiped film evaporator and this type is preferred for distillation in the present process, as the polyalkylene polyether has what may be termed a lubricating action in this type of evaporator in that it assists the passage of the wiper blades over the inner surface of the tube, thus aiding the spreading and agitation of the thin film. Either vertical or horizontal thin film evaporators may be used.

The following may be mentioned as examples of thin film evaporators suitable for use in the present process, the "Luwa" type made by Luwa Ltd., Zurich, Switzerland, the

"Sambay" type made by Samesreuther-Müller-Schuss G.m.b.H. of Butzbach, W. Germany, and the "Kontro" type made by Artisan Industries Inc., of Waltham, Massachusetts, U.S.A.

The distillation process is normally carried out under reduced pressure, preferably at a pressure of 20 mms. of mercury or less. The temperature of distillation will of course be determined by the physical properties of the particular polyisocyanate being recovered but should be kept as low as possible in order to avoid undue exposure to heat.

The polyalkylene polyether may be added to the crude liquid reaction product resulting from the phosgenation of a primary polyamine or salt thereof in an inert diluent and the mixture subjected to a distillation wherein the inert diluent distils first followed by the polyisocyanate. Alternatively the inert diluent may first be removed from the reaction product by distillation before the polyalkylene polyether is added to the polyisocyanate residue and the polyisocyanate recovered therefrom. The process of the present invention may also be carried out on the residue obtained after a portion of the polyisocyanate has already been recovered by distillation. Thus the present process may be applied to any crude organic polyisocyanate from which the polyisocyanate is to be recovered.

The present process leads to the recovery of an increased amount of polyisocyanate over that obtained by normal distillation processes. The present process also leads to the production of a distillation residue which is made more fluid and tractable than heretofore and therefore much more easily removed from distillation apparatus. In most cases it is sufficiently fluid to flow from the still and the necessity for dismantling and scraping out at intervals is minimised.

The invention is illustrated but not limited by the following examples in which all parts and percentages are by weight:

Example 1

To 1,000 g of a 45% solution of crude tolylene diisocyanate obtained by phosgenating a mixture of tolylene 2,4-and 2,6-diamine isomers in o-dichlorobenzene is added 25 g of a polyether of approximate mol. wt. 1,500 made by the reaction of propylene oxide with iso-octanol. The mixture is fed at the rate of 8 g/min. to a vertical wiped-wall thin film evaporator having an evaporative area of approximately 175 sq. cm. operating at 10—12 mm pressure and at a jacket temperature of 178°C.

Distillate amounting to 924 g and containing 430 g tolylene diisocyanate is obtained. This represents a recovery of 95% of the isocyanate feed. Residue amounting to 101 g is produced.

In the absence of polyether it is not possible to operate the thin film evaporator satisfactorily as blockage by solidified residue quickly occurs. The highest jacket temperature which can be used under comparable conditions is 160°C. At this temperature a recovery of 92% of tolylene diisocyanate is obtained, but the residue obtained is of higher melting point than residue containing polyether and is much less tractable.

Example 2

To 44 Kg. of a 48% solution of crude tolylene diisocyanate in o-dichlorobenzene is added 134 g. of a polyether of approximate mol. wt. 1450 made by the reaction of propylene oxide with n-butanol. The mixture is fed during one hour to a Sambay B.160 wiped wall thin film evaporator operating at 10—12 mm. pressure with a jacket temperature of 205°C.

Distillate amounting to 38.5 Kg and containing 20.13 Kg tolylene diisocyanate is obtained. This represents a recovery of 95.3% of the tolylene diisocyanate feed. The residue produced flows readily from the base of the evaporator.

WHAT WE CLAIM IS:—

1. A process for the recovery of organic polyisocyanates from crude mixtures containing said polyisocyanate which comprises mixing a polyalkylene polyether with said crude mixture and distilling the organic polyisocyanate from an agitated thin film of the so-formed mixture of crude polyisocyanate and polyalkylene polyether.

2. A process as claimed in claim 1 wherein the crude mixture is the crude organic polyisocyanate or solution thereof produced by phosgenation of a primary polyamine or a salt thereof.

3. A process as claimed in claim 1 or claim 2 wherein the organic polyisocyanate is an aromatic polyisocyanate.

4. A process as claimed in claim 3 wherein the aromatic polyisocyanate is a tolylene diisocyanate.

5. A process as claimed in any of the preceding claims wherein the polyalkylene polyether is made by the addition polymerisation of 1,2-propylene oxide to a compound containing at least one active hydrogen atom.

6. A process as claimed in claim 5 wherein the polyalkylene polyether is made by addition polymerisation of 1,2-propylene oxide to an aliphatic monohydric alcohol.

7. A process as claimed in claim 6 wherein the aliphatic monohydric alcohol is *n*-butanol.

8. A process as claimed in claim 6 wherein the aliphatic monohydric alcohol is iso-octanol.

9. A process as claimed in any of the preceding claims wherein the amount of

polyalkylene polyether is from 1% to 5% based on the weight of the polyisocyanate.

10. Process as claimed in any of the preceding claims wherein the distillation is carried out in a wiped thin-film evaporator.

11. Process as claimed in any of the preceding claims wherein the distillation is carried out at a pressure of 20 mms of mercury or less.

12. Process according to Claim 1 as hereinbefore described especially with reference to the Examples.

13. Organic polyisocyanates whenever recovered from a crude mixture containing said polyisocyanates by a process as claimed in any of the preceding claims.

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Abingdon: Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1967.
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.